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Published in:
Waste Management

Link to article, DOI:
10.1016/j.wasman.2016.03.040

Publication date:
2016

Document Version
Peer reviewed version

Valorisation of ferric sewage sludge ashes: potential as a phosphorus source

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Abstract

Sewage sludge ashes (SSA), although a waste, contain elements with socio-economic and environmental potential that can be recovered. This is the case of phosphorus (P). SSA from two Danish incinerators were collected during two years and characterized. The sampling was done immediately after incineration (fresh SSA) or from an outdoor deposit (deposited SSA). Although morphology and mineral composition were similar, physico-chemical and metal concentration differences were found between incinerator plants and sampling periods. No differences were observed between deposited and fresh SSA, except for the parameters directly influenced by disposal conditioning (e.g. moisture content). All the SSAs had high concentrations of P (up to 16 wt. %), but they all exceeded Danish EPA Cd and Ni thresholds for direct application at agricultural soil. Fresh and deposited SSA were acid washed aiming P extraction, achieving 50 g P/kg (approx. 37% of total P), but metals were also co-extracted to the liquid phase. To avoid and/or minimize the metals pollution of the extracted P, selective P recovery from the SSA was tested, using the electrodialytic (ED) process. ED laboratory cells, with 3 compartments (3c) and 2 compartments (2c), and two acid concentrations (H_2SO_4, 0.08 M and 0.19 M) were used for 7 days. The most concentrated acid solution increased P solubilization. The 2c-cell combined with the higher acid concentration resulted in higher P recoveries, 125 g of P/kg of SSA in the anolyte. The obtained results showed that the ED process is a valuable tool for the SSA valorisation as it promotes simultaneous P recovery and metals extraction from the SSA.

Keywords: *Electrodialytic process, acid extraction, characterization, phosphorus, metals, recovery*

1. Introduction

Incineration of sewage sludge ash (SSA) is a well-established technology (Werther and Ogada, 1999), being estimated that 300-400 kg of SSA are produced *per* ton of dried sewage sludge (Cyr et al., 2007). During the incineration process, organic contaminants and pathogens are destroyed, while achieving mass reduction, water evaporation and organic matter oxidation to NO_x, SO_x and CO_2. After the incineration in a fluidized bed furnace, exhaust gas fines are collected by electrostatic precipitators or bag filters (Donatello et al., 2010b). Incineration cost is about 210-310 euros *per* ton of dry solids but some controversy arises as this technique promotes potentially hazardous SSA (Smith et al., 2009). In fact, incineration can concentrate up to 13 times the amount of metals when compared to the ones reported in the original matrix (Donatello et al., 2010b; Ottosen et al., 2013).

The SSA are generally considered a waste material to be disposed into landfill (Donatello et al., 2010b), but they can also be reused as adsorbents (Pan et al., 2003), in geotechnical applications (Ferreira et al., 2003) or in construction materials (Al Sayed et al., 1995; Anderson et al., 2002; Lin et al., 2005), since SSA is not considered hazardous waste (Donatello et al., 2010b). Due to the P concentration, typically between 4 and 9% (Biswas et al., 2009; Franz, 2008), fly SSA can be applied at agricultural land, if it complies with the established metal thresholds (e.g. Danish EPA, Miljøstyrelsen). However, as the bioavailability of phosphorus in the SSA is low the untreated ash may not be a suitable fertilizer (Krüger and Adam, 2015; Herzel et al., 2016).

The SSA can be treated aiming P extraction (Donatello et al., 2010a; Franz, 2008; Weigand et al., 2012) using different technologies, e.g. thermal (Adam et al., 2009; Mattenberger et al., 2008; Mattenberger et al., 2010; Vogel et al., 2010), wet treatment process (Petzet et al., 2011; Petzet et al., 2012; Stark et al., 2006) or electrodialytic (ED) separation (Ebbers et al. 2015; Guedes et al., 2014; Ottosen et al., 2014a). An experimental screening of ED P recovery and simultaneous metals removal has been conducted with a 3 compartment (3c) cell (Ebbers et al., 2015; Guedes et al., 2014; Ottosen et al., 2014a), Figure 1a (Jensen and Villumsen, 1995), and 2 compartment (2c) cell (Ebbers et al., 2015; Parés Viader et al., 2015), Figure 1b (Ottosen et al., 2014b). In the 3c cell, the possibility of P extraction from Al-rich and Fe-rich SSA was assessed using acid washing (Ottosen et al., 2013) and the ED process (Ottosen et al., 2014a). Phosphorus separation into the central compartment liquid and the anode compartment ranged between 15-85% for an Al-precipitated SSA and between 45-95% for a Fe-

precipitated SSA. The combination of ED process in the 2c-cell and initial acidification of the stirred suspension with mineral acids showed to be more effective in dissolving P, comparing to the 3c-cell. In the 2c-cell, removals up to 90% (Parés Viader et al. 2015) and 96% (Ebbers et al., 2015) were achieved in 7 days. A previous work reported phosphorus removals up to 70% have been achieved in the anode compartment of a 3c-cell for deposited and fresh Fe-rich SSA of the 3c-cell using 0.08M H_2SO_4 (Guedes et al., 2014). However, neither the 2c-cell setup nor the influence of acid concentration were evaluated.

This work had two main objectives: (i) to evaluate the major differences between SSA collected in different sampling periods, storage conditions and incinerator plants (Lynettefællesskabet and Avedøre Spildevandscenter, Copenhagen, Denmark), and (ii) to assess P recovery from recently collected (fresh) and deposited SSA. This last objective was tested with SSA, collected in the incinerator at Lynettefællesskabet, using a combined acid washing and ED treatment with a 3c and 2c-cell setups.

Please insert Figure 1

2. Experimental

2.1. Sewage sludge ashes

The SSA samples were collected after incineration by fluidized bed combustion at Avedøre Spildevandscenter and Lynettefællesskabet wastewater treatment plants (WWTP), located in Copenhagen, Denmark. The plants treat waste water annually from 345,000 and 500,000 population equivalent, respectively, with no major industrial discharges, prevailing non-industrial wastewater. At both facilities P in the wastewater is precipitated in a Bio-P tank followed by addition of iron salt. After incineration of the sewage sludge, the SSA is collected in electrofilters and the ferric SSA is disposed of in separate landfills for SSA only. In total, 8 samples of SSA were collected. From Avedøre, two samplings (2012 and 2014) were made directly after the electrofilters (fresh). From Lynettefællesskabet, six samples (twice in 2012 and once in 2013) were collected from the electrofilters (fresh) and at the disposal site (deposited). The deposited SSA were collected from the top part of the SSA pile in an open air deposit, and the storage time is unknown. After sampling, the SSA was stored in closed plastic containers at room temperature until the experimental work was carried out.

2.2. SSA characterization

Characterization of the SSA and metals extraction were carried out with oven dried SSA (105 ºC). For all characterization procedures five replicates of each type of SSA were used. Water content of the SSA was calculated as weight loss at 105 ºC for 24 h. The pH was measured in a 1:2.5 (mass:volume) suspension in distilled water using a Radiometer pH electrode. Loss on ignition (LOI) was determined in a muffle at 550 ºC for 30 min. The concentrations of different elements were measured after pre-treatment of the SSA in accordance to DS259 (2003), as 1.0 g of SSA and 20.0 mL (1:1) HNO_3 extracted at 200 kPa, 120 ºC for 30 min and then vacuum filtered through a 0.45 µm filter. Phosphorus, Al, Fe, Zn, Cu, Pb, Cr, Cd and Ni were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

Morphology analysis was performed by scanning electron microscopy supported by energy dispersive spectrometry (SEM-EDX), without pre-treatment of the SSA samples (3 replicates were analysed for each SSA). The accelerating voltage of the SEM was 20-25 kV with large field detector (and X-ray cone). Different areas of the samples were analysed by SEM and the element distribution was examined using EDX. SSA mineralogy was studied by X-ray diffraction (XRD) for the identification of the major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 kV and 40 mA applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-70 2Θ. The diffractograms were interpreted by using the ICDD PDF-4 database for minerals.

2.3. Relation between pH release of metals and P

To determine the pH dependent extraction of P and metals, 10 g dried SSA were suspended in 50 ml HNO_3 of different concentrations (0.00; 0.01; 0.05; 0.08; 0.10; 0.30; 0.50; 0.70 and 1.0 M). The suspensions were placed at an agitating table for 7 days at room temperature. At the end of the experiment, pH was measured and suspensions were filtered by vacuum using 0.45 µm filters and the concentrations determined by ICP-OES. Each extraction was made in duplicate and reference samples were made using distilled water with the same procedure. pH dependent extractions was carried out for the Lynettefællesskabet SSA (2012, 1st sampling).

2.4. ED treatment of SSA

Two ED laboratory cells were used (Figure 1). The cells were made of plastic with an internal diameter of 8 cm, with a suspension compartment length of 10 cm and the electrode compartment of 5 cm. Electrode compartments were separated from the suspension compartment by an anion-exchange membrane and/or a cation-exchange membrane from Ionics (anion exchange membrane, AEM - AR204 SZRA B02249C and cation exchange membrane, CEM - CR67 HUY N12116B). The electrodes were platinum coated titanium from Permascand. A power supply (Hewlett Packard E3612A) was used, maintaining a constant current of 50 mA, corresponding to a current density of 0.08 mA/cm^2, whereas in the 2c-cell was of 0.10 mA/cm^2. The SSA was stirred in the suspension compartment by a flexible plastic flab, coupled to a HETO motor, with a rotation velocity rate of up to 1300 rpm. The SSA was suspended in H_2SO_4 at 0.19 M in the 3c-cell and 0.08 and 0.19 M for the 2c-cell, in the ratio of 1:10 (mass:volume), and 500 mL of 0.01 M $NaNO_3$ was used as electrolyte, with pH adjusted to 2 with 1:1 HNO_3. A total of six ED experiments with SSA from Lynettefællesskabet (2012, 1st sampling), two experiments for each SSA sample (fresh and deposited) were carried out for 7 days with different experimental conditions (Table 1).

During the experiments voltage, current, pH in the electrolytes and pH and conductivity in the SSA suspension were measured. The pH of the electrolytes was manually adjusted to pH between 1 and 2 with 1:1 HNO_3 when necessary.

Please insert Table 1

At the beginning and at the end of each experiment, samples were taken from electrolytes and from the suspension, for P and metal analyses. At the end of the experiments the SSA suspensions were drained through filter paper (grade 113, pore size 30 µm) before drying, to separate the solids from the liquid phase, and water content was measured. Membranes and cathode were soaked in HNO_3 (1 and 5 M, respectively) for 24 hours to release metals for further analysis. The SSA (three replicates), aqueous phases, electrolytes, membranes and cathode were analysed for P and metal contents, using the same ICP-OES.

The removal percentages were calculated by dividing the mass of element removed to different parts of the cell (electrodes, electrolyte solutions and membranes) by the sum of mass found in the different parts of the cell at the end of the experiment.

2.5 Minteq calculations

Visual MINTEQ 3.1 was used to gain further insight into the formation of charged phosphorus complexes which could be transported through the AEM and CEM. For the calculations the chemical composition of the ash liquid solution in experiments after the 7 days with elements present in SSA with Fe as Fe^{3+} or as Fe^{2+} was used. The pH was fixed to the final experimental pH and temperature to 25 °C. The Ionic strength was calculated in the program.

2.6. Statistical analysis

Physico-chemical characteristics, element concentrations in all fresh and deposited SSA were subjected to analysis of variance (ANOVA) and then compared by Tuckey multiple range test at $p < 0.05$. A Student t-test was used for comparison of SSA collected in the same incinerator plant.

3. Results and Discussion

3.1. Chemical characterization of different SSA

The characterization of fresh Avedøre SSA (2012 and 2014) and fresh/deposited Lynettefællesskabet SSA (2012 and 2013) is presented in Table 2.

Regarding physico-chemical characteristics, the changes in pH and conductivity did not follow a specific tendency, differences being attributed to SSA heterogeneity (wastewaters from different urban areas in Denmark but with no major industrial discharges). The high difference in water content between deposited (up to 16%) and fresh (≤ 0.1%) SSA was related to storage (e.g. air humidity, rain). The LOI was generally low (<0.9%), only increasing for one Lynettefællesskabet sample (2.7%). Both plant facilities have thus shown sufficient incineration conditions.

Please insert Table 2

The concentration of the different elements was in the same range in all studied SSA. The P content was generally high in all SSA (between 7 and 16 wt. %). Differences in P are majorly attributed to population diet (Mihelcic et al., 2011), type of wastewater treatment plant system, and type of detergents used. In general, the Zn concentration was higher in Lynettefællesskabet 2012 SSA than in the other samples. In 2014, Avedøre Spildevandscenter had higher concentrations of Cu and Pb than in 2012 or in

Lynettefællesskabet. Again, these variations can be related to the characteristics of the area covered by the WWTP, which directly influence the heterogenous characteristics of the daily SS flows. Most of the studied Danish SSA were in accordance with reported literature ranges (Donatello et al., 2010a; Ebbers et al. 2015; Franz, 2008; Levlin et al., 2003; Ottosen et al., 2013) (also in Table 2, for comparison purposes), except for some samples with higher Zn, Cu and Pb values or lower Fe and Ni concentrations. In this work, Cr levels were below all the concentrations reported in literature.

The Danish EPA has two set of limiting values for metals when spreading waste at agricultural land. The dry matter related concentrations (see Table 1) met the limiting values except for Cd (2.2-3.5 mg/kg) and Ni (35-62 mg/kg) for all SSA, and Pb for one sampling period in Lynettefællesskabet and Avedøre (Table 2). As previously discussed, the pre-treatment of the SSA would significantly improve the amount of P bioavailable for agricultural application.

3.2. Study of SSA from Lynettefællesskabet *(2012)*

Deposited and fresh Lynettefællesskabet SSA from the first 2012 sampling (Table 2) were further analysed, including morphology, mineral composition and potential of acid washing to remove P. These SSA were chosen to deepen the comparison between fresh and deposited SSA.

3.2.1. Morphology and mineral composition

SEM analysis show that the SSA particles generally had irregular shaped (Figure 2) and no major differences were found between fresh and deposited samples. Additionally, SEM/EDX analysis revealed that O, P, Fe, Al, K, Na, Mg, Si, S, and Ca were distributed all over the particle surfaces in both SSA.

Please insert Figure 2

The mineralogy of fly SSA generally represents an assemblage of crystalline and amorphous phases (Bayuseno and Schmahl, 2011). The major mineral phases identified by XRD are presented in Figure 3 and show differences between deposited and fresh SSA. Silicon oxide in the form of quartz (SiO_2) was identified in both SSA, agreeing with published data for other SSA (Cyr et al., 2007) where Si is likely to be present in its crystalline or amorphous phase. Phosphates on both SSA were indicated as calcium

239 phosphates, but the only chemical formula clearly identified was as whitlockite
240 [$Ca_9(MgFe)(PO_4)_6PO_3OH$]. Hematite (Fe_2O_3) was also identified, being the iron oxide a
241 consequence of SS incineration (800-900 ºC) in excess air which promotes the existence
242 of metals as oxides (Donatello et al., 2010b).
243
244 **Please insert Figure 3**
245
246 There was $CaSO_4$ in both samples, however difficult to completely identify. In the fresh
247 sample, it is likely present as anhydrite ($CaSO_4$) and in the deposited, it was not clear,
248 although not anhydrite nor gypsum ($CaSO_4 \cdot 2H_2O$). However, anhydrite can be present
249 in SSA when they are fresh but as a result of "hydration" of the SSA, gypsum may start
250 to form (Bayuseno and Schmahl, 2011), though this was not confirmed by XRD in the
251 present work. In SEM/EDX a S rich region was observed and can belong to i) an
252 amorphous $CaSO_4$ or ii) $Na_2SO_4/K_2SO_4/NaKSO_4$ condensed on this Ca-rich particle.
253 The amorphous phase in other SSAs is between 40-74% (Cyr et al., 2007). In this case,
254 from XRD patterns of fresh and deposited SSA samples it can be inferred that some
255 amorphous phases are present due to the slight hump between 2θ of 10 and 30˚ but the
256 material is not prevalently amorphous.
257 A semi-quantitative method, Reference Intensity Ratio (RIR), based on the diffraction
258 intensity of the strongest peak of a given phase in comparison with corundum, was used
259 to indicate the relative mineral mass fractions in the two SSA. The RIR method
260 indicated that the mass distribution of the major crystalline phases in both SSA were as
261 following: calcium phosphate and quartz > iron oxide and calcium sulphate.
262
263 ***3.2.2. Acid washing of SSA***
264 The percentage of P extracted from the SSA as a function of pH is shown in Figure 4.
265 Storage did not affect the extent of P extraction even at the strongest concentration, 1.0
266 M, where more than 50 g/kg were extracted. This 40% of total P mobilization is in
267 accordance with the average percentage reported in other works, for the same pH
268 (Ottosen et al., 2013). A pH decrease, other L/S ratios or extracting agents could have
269 increase the total amount of mobilized P (Ottosen et al., 2013).
270 Regarding storage, the release of a specific element as a function of pH is very similar
271 for fresh and deposited SSA, except for a slight variation of Cd at pH between 2 and 3.
272 The major mineralogy of the material and the phases controlling the solubility of major

trace elements (as suggested by the results of mineralogy test) were also not affected, neither the amount of elements extracted. Instead, extraction is mainly correlated with pH changes, particularly at low pH values. At low pH values the solubilized percentages were: Zn 65%, Cu approx. 55%, and less than 33% Ni and Al (Figure 4). Iron was bound strongly in both SSA, and even at the lowest pH, less than 2% was solubilized. This is in accordance to what was expected as Fe_2O_3, which is insoluble in acid (Donatello et al., 2010b), was identified in larger quantities in both SSA. The XRD investigation also showed the presence of $Ca_9(MgFe)(PO_4)_6PO_3OH$ in the SSA. But, since at low pH, only a small amount of Fe was extracted in contrast to more than 35% of P in both samples (Figure 4) these two elements may have not been associated in the SSA, even though Fe was originally used for precipitation of P during the wastewater treatment. As metals mobilization started approximately at the same pH than P mobilization, the obtained acidic liquid solution was a mixture between P and metals, and a further separation step is needed.

Please insert Figure 4

3.2.3. Electrodialytic treatment

3.2.3.1. Mass balance

Mass balance of an element was defined as the relation between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration. The mass balances for the elements presented high variability for all the experiments. An inhomogeneous distribution of metals in the ash and, consequently, imperfect mass balances are expected when working with these type of samples. Finally, even though careful handling of all samples the precipitation of insoluble compounds may occur in e.g. set-up tubing. Mass balance in the different experiments varied between 80–120% with no linear tendency.

3.2.3.2. Electrodialytic P-separation

Table 3 shows the initial conditions and the changes in pH, conductivity and mass loss after the ED experiments. Before the experiment the SSA was suspended in sulphuric acid (0.08 and 0.19M) aiming to convert the precipitated and adsorbed P into mobile

ionic forms able to electromigrate during the ED treatments. The initial pH in the central cell compartment varied between 1.0 and 2.6 for the SSA (Table 2). During the ED experiments, pH in the SSA compartment slightly decreased in the 3c-cell and continued to decrease in the 2c-cell due to the generation of H^+ in the anode compartment. Water splitting at the AEM may have also contributed for the acidification. The dissolution of ash particles during the ED treatment results in a mass loss that can be quite significant (Guedes et al., 2014; Ottosen et al., 2006) as it can be seen in Table 3. In the 2c-cell experiments there was a conductivity increase at the end of the experiments. This is due to the electrolysis at the anode and solubilisation of SSA ions that are not transported out of the suspension as fast as produced. In the 3c-cell the solubilized ions from the SSA suspension are migrating either to the anode or cathode compartments. Consequently, the central compartment is being depleted from ions, which decreases the conductivity of the suspension.

Please insert Table 3

In the ED cells, the released metals are expected to be found as positively charged species whereas the solubilised P is more likely to be found in negatively charged or neutral species at acidic pH (H_3PO_4, $H_2PO_4^-$), except for Al-P, Ca-P and Fe-P complexes formation. In the 3c-cell the main objective is to dissolve and mobilize the P from the SSA suspension (central compartment) to the anode compartment and the metals to the cathode compartment. In the 2c-cell the aim is to dissolve P and metals from the SSA keeping P in the suspension (anolyte) whereas the metals are removed into the cathode compartment. Afterwards the ED treatment using the 2c-cell, the suspension (anolyte) is filtered, being the P rich filtrate cleaned from ash particles.

In this study, a more concentrated H_2SO_4 solution was used in the 3c-cell compared to the previous work where 0.08 M solution was used (Guedes et al., 2014). The increase in the acid concentration improved P solubilization by 17% (experiments F-3-0.19 and D-3-0.19, Figure 5). In total between 24.9 and 29.4% of P were removed to the anolyte of the 3c-cell, mainly as $H_2PO_4^-$ (Table 4), whereas in the previous work 17.9 and 18.8% were removed to the anolyte after 7 days (Guedes et al., 2014).

Please insert Figure 5

When the 2c-cell with 0.08 M of H_2SO_4 was used 91% of P for F-2-0.08 and 67% for D-2-0.08 were solubilized. From these, 14 and 11% of P (F-2-0.08 and D-2-0.08, respectively) electromigrated to the cathode compartment, probably due to the complexation with Al, Fe and Ca forming positively charged species like $AlHPO_4^+$, $CaH_2PO_4^+$ and $FeH_2PO_4^{2+}$ (Table 4). At the end, the anolyte solution still contained 77% of P in F-2-0.08 and 56% in D-2-0.08 (Figure 5) being mainly present as H_3PO_4 and $H_2PO_4^-$ (Table 4). In the acid washing test, this difference in P solubilization was not observed. One hypotheses is that deposited SSA sample used in the experiment D-2-0.08 may have contained more acid-insoluble P-complexes (samples heterogeneity) influencing the results. Still, in these two experiments, the type of SSA influenced the total P solubilization by the different setups and, consequently, the amount collected in the anolyte solution. In this case, the best option may be to use ash collected immediately after incineration. The increase in the acid concentration in the 2c-cell set-up resulted in higher P solubilization from the SSA, approx. 99% in both cases. From these, 93 and 97% in the F-2-0.19 and D-2-0.19, respectively, remained in the anolyte as H_3PO_4 and $H_2PO_4^-$ (Table 4). Only 7% in F-2-0.19 and 2% in D-2-0.19 electromigrated toward the cathode compartment mainly as Al, Ca, and Fe complexes ($AlHPO_4^+$, $Al_2PO_4^{+3}$, $CaH_2PO_4^+$, $FeH_2PO_4^{2+}$ and $FeHPO_4^+$, Table 4).

In terms of metals, generally, higher removals were achieved when 0.19M of H_2SO_4 was used compared to the use of 0.08M, independently of the cell design (3c-cell or 2c-compartment). The metals solubilization after the 7 days of experiment were:

- Fe (9%) < Pb (14%) < Cr (16%) = Ni < Zn (56%) < Al (57%) < Cu (69%) < Cd (82%) for F-3-0.19
- Pb (10%) < Fe (12%) < Cr (20%) < Ni (36%) < Al (44%) < Zn (73%) < Cu (76%) < Cd (82%) for D-3-0.19
- Pb (7%) < Fe (10%) < Cr (11%) < Ni (16%) < Cd (18%) < Al (53%) < Cu (55%) < Zn (64%) for F-2-0.08
- Pb (9%) < Fe (12%) = Cr < Ni (17%) < Cd (23%) < Al (42%) < Cu (44%) < Zn (51%) for D-2-0.08
- Fe (6%) < Cr (10%) < Pb (12%) < Ni (13%) < Cd (23%) < Al (53%) = Zn < Cu (69%) for F-2-0.19
- Fe (8%) < Pb (14%) < Cr (16%) < Ni (18%) < Cd (27%) < Zn (51%) < Al (61%) < Cu (64%) for D-2-0.19

The exception was Cd which solubilization was higher in the 3c-cell, 82% in both experiments (F-3-0.19 and D-3-0.19) contrasting to the 23 and 27% in the F-2-0.19 and D-2-0.19, respectively. In the 2c-cell experiments, between 73-82% of Cd remained in the ash whereas in the 3c-cell the value was 18%. Although unclear, a possible explanation is that the reactions that occurred in the anode end, where the SSA is placed, might have affected the Cd solubilization (e.g. precipitation) and this should be further investigated. Still, higher solubilization values for Cd (89%) were obtained by Ebbers et al. (2015) using a 2c-cell with 0.19 M of H_2SO_4.

As Fe and Pb are tightly bounded to more insoluble ashes particles (Ottosen et al., 2014a) neither the increase in the acid concentration nor the change in the cell design improved their removals.

Comparing to the previous work (Guedes et al., 2014) generally, higher percentages were solubilized from the SSA in these experiments (F-3-0.19 and D-3-0.19) due to the increased acid concentration, 0.19 M. Between more 3% (Fe in the fresh SSA) and 36% (Cd in the deposited SSA) were solubilized from the SSA comparing to the results obtained with 0.08 M (Guedes et al., 2014). No differences were found for Al in the deposited SSA (D-3-0.19) and Cr and Cu in the fresh SSA (F-3-0.19).

Please insert Table 4

3.2.5. Techniques comparison

At the end of all ED experiments pH was between 1.9 and 1.2. Through comparison to acid washing, it was expected that at least 35% of P had been solubilized from the SSA in the ED cells (Figure 4) staying in the anode compartment in the 2c-cell or electromigrating to anode compartment in the case of the 3c-cell. In all cases, the amount of P solubilized was higher in the ED cell (generally higher than 80%, except in D-2-0.08 that was 67%) than in the acid washing. This may be attributed to four factors: (i) the use of sulphuric acid in the ED treatment, instead of the nitric acid used in the acid washing; (ii) the combination of an increased solubilisation of P compounds, due to equilibrium displacement by Al, Ca and Fe cations migration into the catholyte (Parés Viader et al., 2015); (iii) a higher liquid-to-solid ratio (L/S) in the ED remediation (L/S=10) than in the acid extraction experiments (L/S=5); and (iv) the continuous generation of H^+ ions (either by water electrolysis or water splitting). The main

advantage of the ED process comparing to acid washing is the simultaneous extraction and separation of P from the other element in the ash, namely the metals.

Between cell designs, the use of a 2c-cell setup increased overall efficiency of P recovery after 7 days of experiment, under the conditions here tested. Although the applied current was the same (50 mA) the corresponding current density was different (0.08 mA/cm^2 in the 3c-cell *vs* 0.10 mA/cm^2 in the 2c-cell) which may have influenced the results. Also, P dissolution seems to be faster and more complete in the 2c-cell experiments than in the 3c-cell, possibly due to the faster formation of H^+ ions due to water electrolysis. Another important factor is that, at the end of experiments, the P that stays in the suspension of the anode compartment (anolyte) in the 2c-cell (either as uncharged species or anions) is accounted as recovered whereas in the 3c-cell the amount of P that stays in the central compartment liquid (as neutral species) is not considered recovered. At the end, and though the amount of P solubilized in the 3c-cell and 2c-cell using 0.19 M of H_2SO_4 was very similar (approx. 92% and 99%, respectively), the P recovered was only 25-29% in the 3c-cell contrasting to the 93-97% in the 2c-cell. Still, in the 2c-cell set-up, the P was not completely separated from the metals as it can be seen in Table 5 (for example, 32% of Al for F-2-0.19 and 45% for D-2-0.19 are still in the anolyte). From the total amount of elements analysed, the anolyte solution of D-2-0.19 was constituted by 90% of P and 10% of metals, whereas F-2-0.19 anolyte contained 93% of P and the remaining 8% were metals.

Please insert Table 5

4. Conclusions

The SSA from Avedøre and Lynettefællesskabet incinerator plants showed no large differences between their chemical characteristics, except for those related with SSA heterogeneity. Additionally, samples collected at different stages (fresh and deposited) at the same incineration plant showed no trending differences in metal content and physico-chemical parameters. The exception was the moisture content, which was directly related with the disposal conditions.

All the SSA exceeded Danish EPA Cd and Ni thresholds regarding agriculture application. Their high P concentration (up to 16 wt. %) justifies the need of P recovery. More than 50 g of P/kg was extracted from fresh and deposited Lynettefællesskabet SSA (2012) by acid washing, together with a high amount of metals.

The ED process proved to be a viable option for simultaneous extraction and separation of metals and P thus promoting the valorization of the SSA. The use of a 2c-cell to solubilize and separate P from the metals seems to be the best option with the best results being achieved when 0.19 M of H_2SO_4 were used (up to 99% of P solubilization). In total, approx. 125 g of P/kg of SSA were recovered in the anolytes showing that the SSA are valuable P sources. However, the optimization of the ED conditions, current and duration, are still needed aiming at decreasing energy costs.

Although more tests are needed, the type of ash used in the process may influence P recovery, and it needs to be taken into account. In this study, the SSA collected after the incineration allowed to recover more 24% of P than the use of the SSA collected from the deposit, when the 2c-cell with 0.08 M of sulfuric acid was used.

Acknowledgements

Authors would like to thank Ebba C. Schnell, Sabrina Madsen, Christina W. Dufke for laboratorial support and analysis, as well as Lynettefællesskabet for providing the SSA samples. Morten Reiff, Morten G. Meldgaard, Asger B. Carlsen, Søren R. Petersen, Christine Rem, Jeppe Søbye Andreasen, Leander Jørgensen, Gonca Kurt, Liv Rosenmai and Sabine Svendsen are thanked for all their experimental and analytical work. Cátia Magro is acknowledged for statistical analysis. Financial support for the work was provided by projects FP7-PEOPLE-2010-IRSES-269289-*ELECTROACROSS* and PTDC/ECM/111860/2009. N. Couto also thanks *Fundação para a Ciência e a Tecnologia* for her Post-Doc fellowship (SFRH/BPD/81122/2011).

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Highlights

- Sewage sludge ashes fresh and deposited were studied aiming phosphorus recovery
- Ashes physico-chemical differences depended on incinerator plant and sampling date
- Phosphorus solution after acid wash contained high amount of heavy metals
- The 2 compartment ED-cell improved phosphorus extraction and recovery
- A cleaner phosphorus solution was obtained after ED

Figure 1

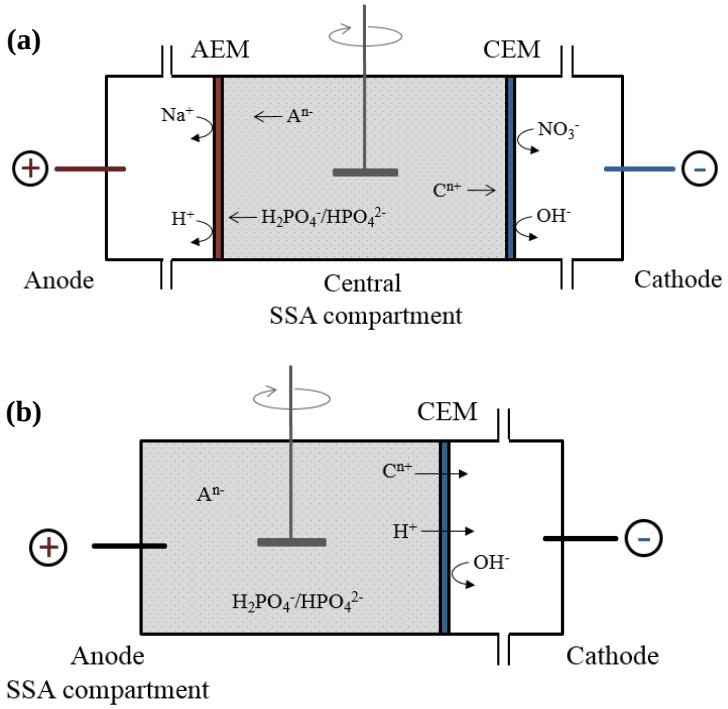

Figure 1. Schematic view of (a) 3-compartment and (b) 2-compartment electrodialytic laboratory cell. (CEM: cation exchange membrane; AEM: anion exchange membrane)

Figure 2

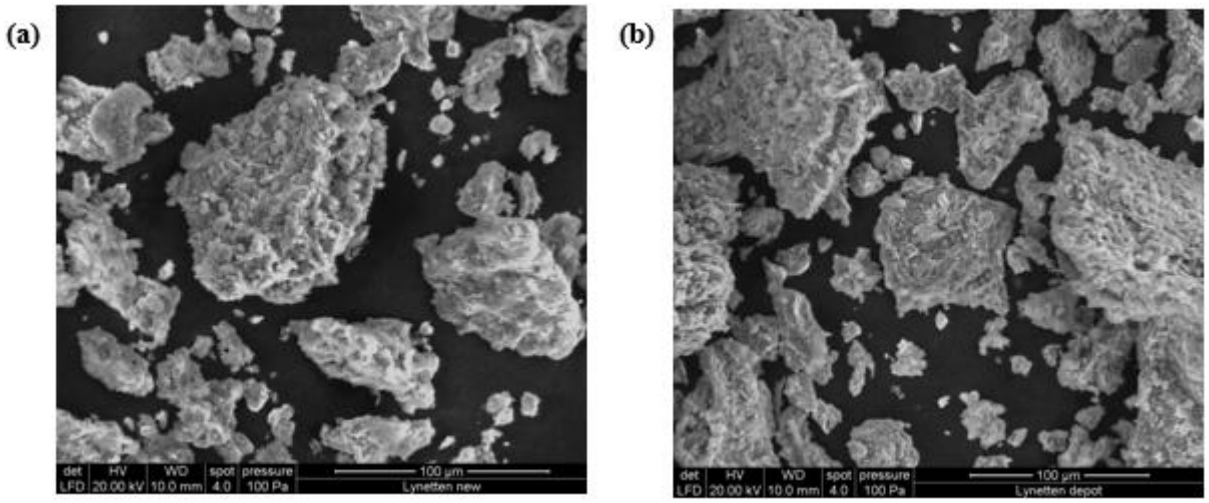

Figure 2. SEM micrographs of (a) fresh and (b) deposited Lynettefællesskabet SSA 2012 1st sampling.

Figure 3

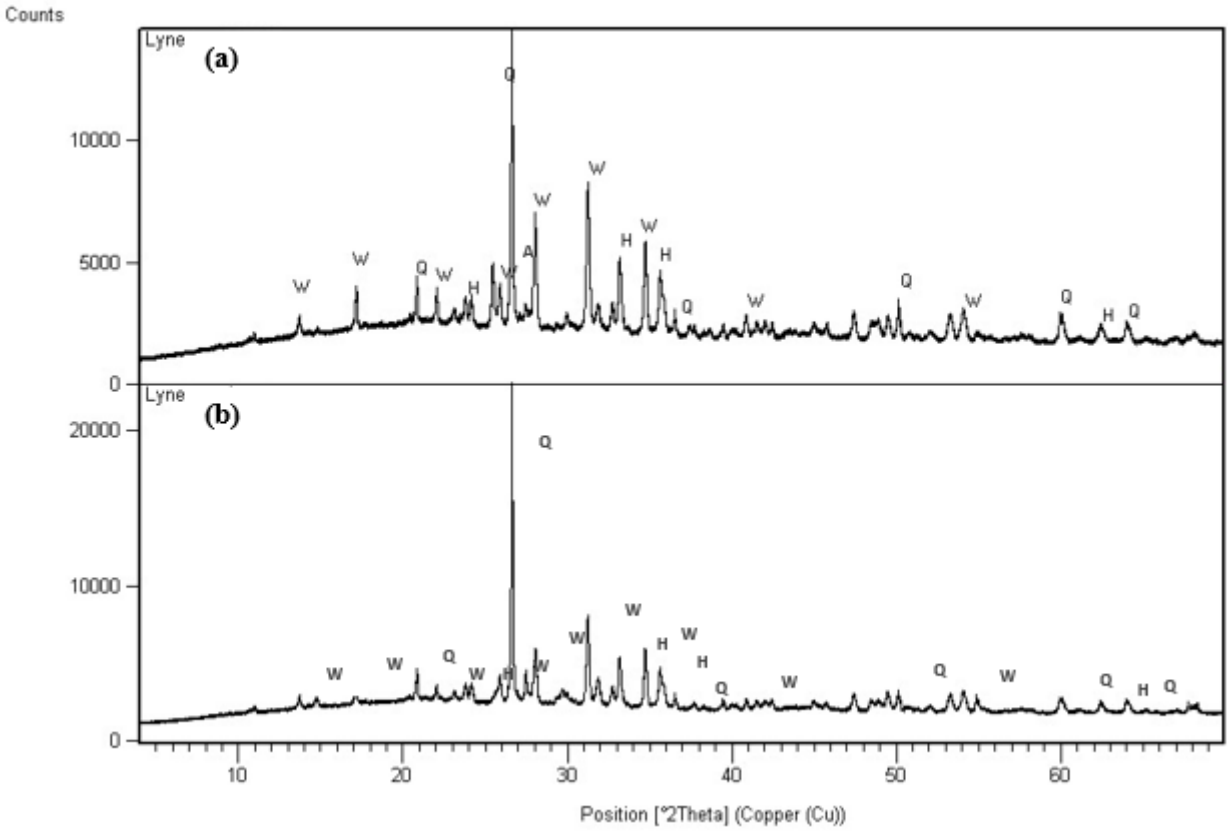

Figure 3. XRD diffractograms of (a) fresh and (b) deposited Lynettefællesskabet SSA 2012 1st sampling (Q - Quartz, W- Whitlockite, H – Hematite, A – Anhydrite).

Figure 4

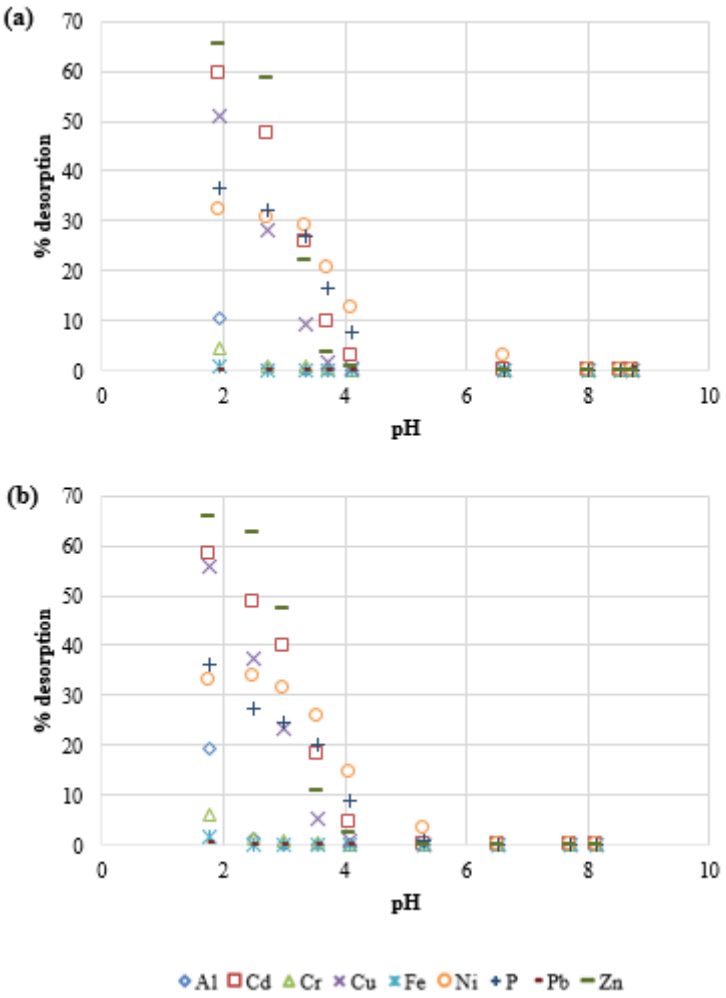

Figure 4. Phosphorus and metal extraction as a function of pH in batch extraction experiments on (a) fresh and (b) deposited SSA Lynettefællesskabet 2012 (1st sampling) using HNO_3.

Figure 5

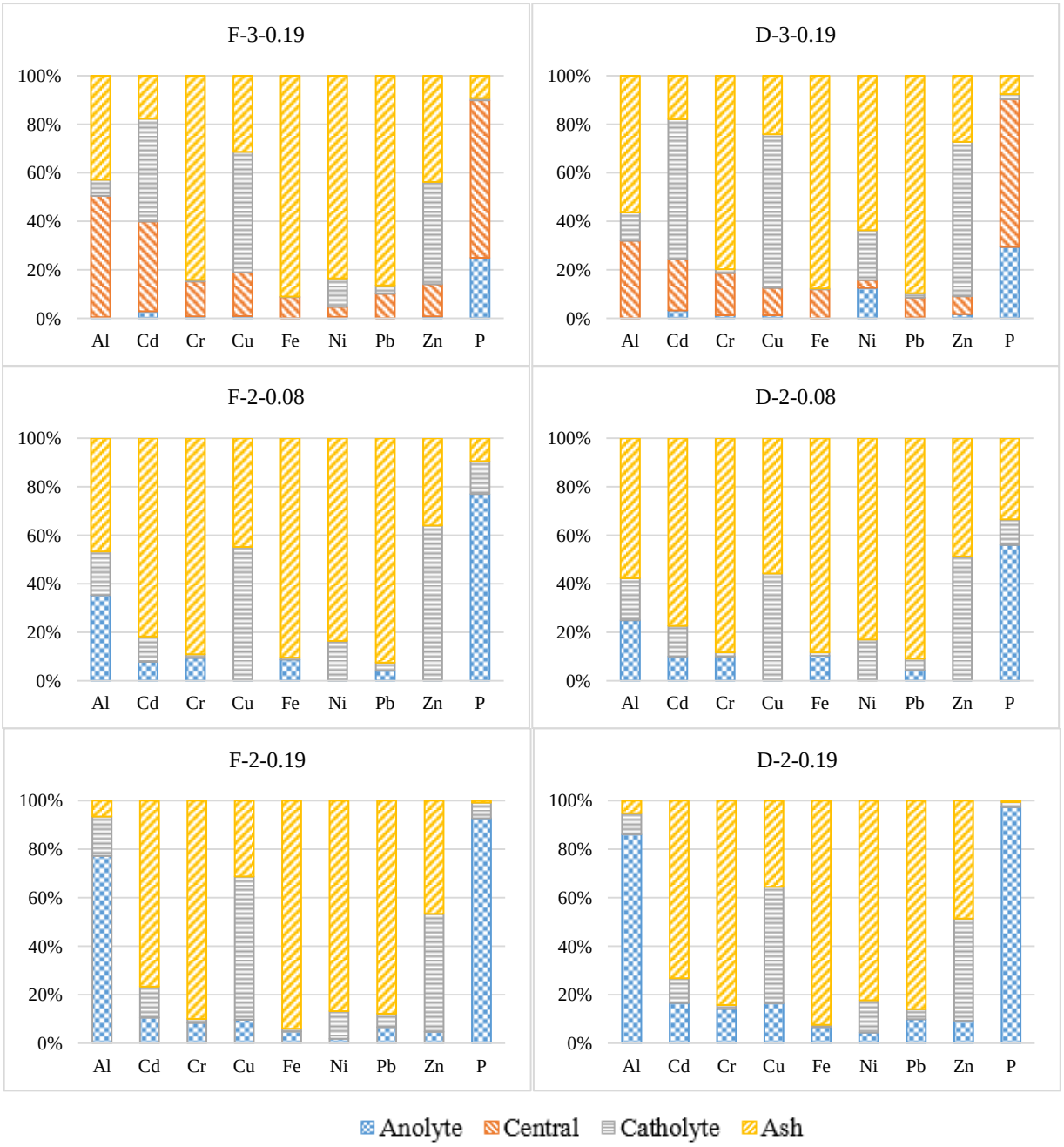

Figure 5. Percentage of heavy metals and phosphorus in the different matrices after the ED treatment in the 3C and 2c-cell design.

Table 1. Experimental design for the Lynettefællesskabet SSA (2012, 1st sampling).

Experiment	Lynetten SSA sample	Cell design	SSA compartment	H_2SO_4 (M)
F-3-0.19	Fresh (2012)	3 compartment	central	0.19
D-3-0.19	Deposited (2012)			
F-2-0.08	Fresh (2012)	2 compartment	anode	0.08
D-2-0.08	Deposited (2012)			
F-2-0.19	Fresh (2012)			0.19
D-2-0.19	Deposited (2012)			

Table 2

***Table 2**- Characteristics of the studied Danish SSA including heavy metal concentrations in relation to the total dry mass (mean ± STD) and limiting values for spreading at agricultural land. Values reported in literature were also used for comparison.*

		Lynettefællesskabet						***Avedøre***		**Limiting values (mg/kg) [a]**	***Literature [b]***
		2012 (1st sampling)		***2012 (2nd sampling)***		***2013***		***2012***	***2014***		
	Parameter	***Fresh* (1)**	***Deposited* (1)**	***Fresh***	***Deposited***	***Fresh***	***Deposited***	***Fresh***	***Fresh***		
Physical and chemical characteristics	pH (H_2O)	12.44 ± 0.01 *#	8.85 ± 0.03 *	12.4 ± 0.05 *#	8.3 ± 0.03 *	12.6 ± 0.02 #	12.6 ± 0.01 #	10.4 ± 0.0 *	9.6 ± 0.10 *		
	Water content (%)	0.10 ± 0.18 *	16 ± 0.38 *	0.09 ± 0.03	14.4 ± 0.09	3.70 ± 0.04 #	3.93 ± 0.07 #	-	0.16 ± 0.01		
	Conductivity (mS/cm)	3.23 ± 0.51 *	4.81 ± 0.13 *#	7.81 ± 0.02 *	5.59 ± 0.11 *#	10.54 ± 0.21 #	9.97 ± 0.82 #	2.12 ± 0.02 *#	2.52 ± 0.14 *#		
	Loss on ignition (550 ºC; %)	0.15 ± 0.05 *#	0.92 ± 0.08 *	0.25 ± 0.05 *#	0.16 ± 0.00 *	2.58 ± 0.01 *	0.47 ± 0.04 *	0.3 ± 0.1 *#	0.57 ± 0.07 *		
	Solubility in water (%)	1.8 ± 0.1 *	3.1 ± 0.0 *	5.12	0.84	5.3 ± 0.0	5.6 ± 0.79	-	29.5		
	Gas production (mL gas/g)	1.6 ± 0.1	1.9 ± 0.2	-	-	-	-	-	-		
Elements	P (g/kg)	134 ± 1	130 ± 5	161 ± 12	-	72.5 ± 0.01 *	68.3 ± 1.5 *	112 ± 2 #	105.4 ± 3.8 #		39-123
	Al (g/kg)	22.6 ± 0.5 *	21.5 ± 0.7 *	21.2	19.5	14.2 ± 0.0	-	20.3 ± 0.5 *	22.1 ± 0.6 *		19.7-218
	Fe (g/kg)	60.0 ± 1.4	62.0 ± 2.3	44.0	-	36.3 ± 0.1	-	78.2 ± 2.9 *	53.2 ± 1.5 *		47-200
	Zn (mg/kg)	3335 ± 77 *#	3157 ± 128 *	3060 ± 222 #	2810 ± 117	2414 ± 10 *#	2270 ± 66.7 *#	2160 ± 60 *#	2410 ± 72 *#	***4000***	448-2737
	Cu (mg/kg)	758 ± 4.9 *	733 ± 9 *	711 ± 5.65 *	694 ± 6.49 *	512 ± 4 #	507 ± 7.58 #	550 ± 10 *	815 ± 18 *	***1000***	417-690
	Pb (mg/kg)	293 ± 44 #	297 ± 9	102 ± 2.15 #	99.5 ± 1.08 #	102 ± 2 #	98.8 ± 5.44 #	90 ± 1 #	253 ± 181 #	***120***	18-158
	Cr (mg/kg)	45.5 ± 0.4 #	44.9 ± 0.7 #	29.7 ± 0.66	28.6 ± 0.61	45.0 ± 0.5 #	44.9 ± 0.40 #	80 ± 2 *	47 ± 1 *#	***100***	102-136
	Cd (mg/kg)	3.25 ± 0.04 #	3.14 ± 0.08	2.21 ± 0.05	2.16 ± 0.09 #	2.2 ± 0.1 #	2.2± 0.1 #	3.4 ± 0.1 #	3.54 ± 0.35 #	***0.8***	0.4-3.9
	Ni (mg/kg)	54.6 ± 0.6	55.7 ± 1.0	35.2 ± 0.72	35.4 ± 0.58	38.9 ± 0.6	37.8 ± 0.14	60 ± 1	62 ± 1.6	***30***	50-93

NOTES:
* indicate statistically significant differences among pairs (columns with some colour) ($p < 0.05$) – t-test
# indicate the absence of statistically significant differences inside the group of non-deposited and deposited SSA ($p < 0.05$) – ANOVA
[a] Danish EPA (Miljøstyrelsen)
[b] [5, 12, 14, 24, 28]
(1) samples used in the experiments aiming P-recovery (acid washing and ED process).

Table 3. Parameters measured at the beginning and at the end of the electrodialytic experiments.

Experiment	Voltage drop (V)		SSA suspension [1]				Mass loss (%)
			pH		Cond. (mS/cm)		
	Start	End	Start	End	Start	End	
F-3-0.19	5.1	4.2	2.25	1.61	22.2	11.7	41
D-3-0.19	6.8	4.4	2.04	1.84	32.4	13.2	40
F-2-0.08	6.7	4.3	2.63	1.68	9.6	22.5	43
D-2-0.08	5.7	4.7	2.47	1.55	14.1	32.8	41
F-2-0.19	5.0	4.5	2.11	1.28	15.9	32.6	42
D-2-0.19	4.8	4.7	2.80	1.24	26.7	33.3	36

[1] Central compartment in the 3 compartment cell and anode compartment in the 2 compartment cell

Table 4

Table 4. MINTEQ calculation of major species of phosphate ions (%) for concentrations of elements in the the ash suspension liquid at the end of the treatments.

	Experiments	**F-3-0.19**		**D-3-0.19**		**F-2-0.08**		**D-2-0.08**		**F-2-0.19**		**D-2-0.19**	
	Fe oxidation state	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
P	$H_2PO_4^-$	22.6	21.2	28.8	27.2	27.6	27.6	22.8	22.6	14.6	14.2	13.7	13.3
	H_3PO_4	55.3	51.4	42.3	39.8	57.4	57.1	67.2	66.6	73.7	71.6	76.5	74.2
	$AlHPO_4^+$	4.62	4.28	7.73	7.28	4.50	4.44	2.29	2.23	1.73	1.68	1.39	1.34
	$Al_2PO_4^{+3}$	0.35	0.32	0.69	0.66	0.27	0.27	0.07	0.06	0.08	0.08	0.06	0.05
	$CaH_2PO_4^+$	4.48	4.17	5.77	5.43	5.96	5.92	3.17	5.92	3.71	3.62	2.84	2.76
	$FeH_2PO_4^{2+}$	12.6	12.9	14.6	10.9	4.31	3.09	4.48	3.75	6.17	7.30	5.55	7.05
	$FeHPO_4^+$	-	-	-	8.68	-	-	-	1.64	-	1.49	-	1.33

Table 5

Table 1. Mass of element removed to the anolyte *per* kg of ash at the end of the electrodialytic experiments (mg/kg).

Elements	F-3-0.19	D-3-0.19	F-2-0.08	D-2-0.08	F-2-0.19	D-2-0.19
P	33334.7	37879.6	102978.0	72153.4	124054.5	125420.4
Al	86.3	54.3	7957.8	5346.9	7148.3	9592.1
Cd	0.1	0.1	0.3	0.3	0.3	0.5
Cr	0.4	0.4	4.3	4.5	3.8	6.4
Cu	6.3	9.3	0.0	0.0	72.9	120.4
Fe	27.1	59.1	5246.1	6410.9	2867.8	4114.6
Ni	0.3	7.0	0.0	0.0	1.0	2.4
Pb	0.1	0.9	12.0	13.0	19.5	29.1
Zn	24.3	53.3	0.0	1.1	155.8	291.7